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CVD - siloxanes Film

(54) **Process for forming cvd SiO2 film with polysiloxane/ozone reaction and semi-conductor device.**

(57) In a process for forming a CVD film, a polysiloxane compound having at least two silicon-oxygen bonds is reacted with ozone to form an SiO_2 film. If desired, the reaction may be effected in the presence of a gas containing an impurity mixed with the polysiloxane compound and ozone to form a PSG, BSG or BPSG film. In a semiconductor device, the SiO_2 film, or the PSG, BSG or BPSG film is used as a planarizing film, an interlayer insulating film, or a cover insulating film.

EP 0 436 185 A1

PROCESS FOR FORMING CVD FILM AND SEMICONDUCTOR DEVICE

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a process for forming a CVD (chemical vapor deposition) film and a semiconductor device, and more particularly to a process for forming an insulating film such as an SiO_2 film according to a CVD method and a semiconductor device using such a CVD film.

The multi-layer wiring technology has been in progress as a powerful means for increasing the scale of integration of semiconductor devices. In keeping with this, development of a method of forming an interlayer insulating film which is most adaptable for a multi-layer wiring structure has been increasingly in demand. In order to eliminate disconnection of metallic wirings because of stress migration and minimize the strain of devices and the like because of thermal stress, there has recently been a demand for development of a process capable of forming an interlayer insulating film at as low a temperature as possible.

Prior Art

Various proposals have heretofore been made of processes for forming an SiO_2 film according to a chemical vapor deposition method (hereinafter referred to as a "CVD method"), among which representative processes capable of forming an SiO_2 film at a low temperature in particular include those mentioned below.

(1) SiH_4-O_2 Process

This is a process for depositing an SiO_2 film on a semiconductor substrate at a temperature of 350 to 450 °C according to a reaction represented by the following formula: $SiH_4 + SiO_2 \rightarrow SiO_2 + 2H_2$. This reaction occurs in a gaseous phase, and hence an SiO_2 film is formed through simple deposition.

Acccording to this process, a large number of particles are liable to be generated to deteriorate the quality of the resulting film and liable to give rise to uptake of moisture into the film, presenting a problem of poor reliability. Furthermore, the poor step coverage of the film entails a problem of disconnection of wirings formed on the film. Moreover, special care must be taken of SiH_4 as a reactive gas to be used in the reaction because of its self-burning properties. This makes the handling of SiH_4 complicated.

(2) Plasma CVD Process Using SiH_4-N_2O or Like

This method is advantageous in that an SiO_2 film can be formed at a temperature as low as 300 to 400 °C. However, since it is a film formation process utilizing charged particles, damage to a device is so great that the process is unsuitable for use in production of very fine devices and VLSI structures. Furthermore, plasma discharge is so liable to break down all kinds of chemical bonds that a good-quality film can not always be obtained. Moreover, the process involves generation of a large number of particles and a great possibility that metallic atoms and the like constituting the inside of a reaction chamber used in the process may be incorporated into the resulting film to cause contamination of the film. In addition, the film obtained by the process has a problem of poor step coverage.

(3) TEOS-O_3 Process

This is a process wherein TEOS (tetraethyl ortho-silicate, $Si(OC_2H_5)_4$, an alkoxysilane) is decomposed with the aid of O_3 (ozone) to form an SiO_2 film.

This method has various advantages such as safety of TEOS, good step coverage, little generation of particles, and other merits in association with the reaction rate determination of surface. Accordingly, this process can eliminate the defects of the above-mentioned SiH_4-O_2 process (1) and plasma CVD process using SiH_4-N_2O and the like (2).

In accordance with the process for forming an SiO_2 film according to the TEOS-O_3 reaction, however, the deposition rate of an SiO_2 film is dependent upon the O_3 concentration, while the film quality thereof is not always satisfactory and the step coverage of the film around stepped portions of the underlying surface turns from flowing profiles into isotropic profiles as the O_3concentration is decreased (about 3 mol % or less). This entails a difficulty in using such SiO_2 films as interlayer insulating films.

Furthermore, when the underlying surface is of a thermal SiO_2 film, the unevenness, or roughness, of the surface of an SiO_2 film formed thereon by the TEOS-O_3 process increases with an increase in the O_3 concentration to increase the possibility of causing failures such as disconnection of wirings.

Moreover, the TEOS-O_3 reaction involves a high possibility of particle generation because it is not necessarily a perfect surface reaction.

ming an SiO_2 film according to the TEOS-O_3 reaction, the film quality, the step coverage, the film surface state, the film deposition rate, etc. are so dependent upon the O_3 concentration that SiO_2 films cannot always be formed stably.

The present invention has been made in view of the foregoing problems of the prior art. Accordingly, an object of the present invention is to provide a novel CVD process easy of production control with a constant deposition rate and capable of forming a good-quality CVD film with good step coverage and other characteristics.

SUMMARY OF THE INVENTION

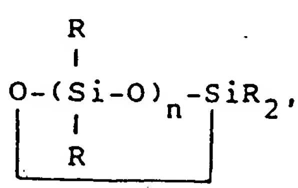
In accordance with the present invention, there is provided a process for forming a CVD film, comprising reacting a polysiloxane compound having at least two silicon-oxygen bonds with ozone to form an SiO_2 film.

Examples of the polysiloxane compound having at least two silicon-oxygen bonds include linear siloxane compounds represented by the following formula:

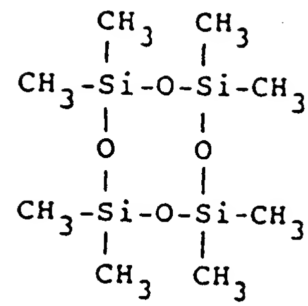
$$R_3Si-(\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-O)_n-SiR_3,$$

which include hexamethyldisiloxane.

Other examples of the polysiloxane compounds having at least two silicon-oxygen bonds include cyclic siloxane compounds represented by the following formula:



which include octamethylcyclotetrasiloxane (OMCTS) represented by the following molecular formula:



and hexamethylcyclotrisiloxane.

In the above-mentioned formulae, R stands for an alkyl group which includes no hydrophilic substituent groups such as

$$-OH,\quad -\underset{\underset{O}{\|}}{C}-OH,\quad -CHO,\ \text{and}\ -\underset{\underset{CH_3}{|}}{C}=O,$$

provided that a number of R groups in one compound molecule may be the same or different.

When a PSG film, a BSG film or a BPSG film is to be formed by the CVD process of the present invention, the above-mentioned polysiloxane compound having at least two silicon-oxygen bonds is mixed with a gas containing an impurity such as phosphorus or boron to be reacted with ozone.

The CVD process of the present invention has the following features:

(1) The reaction does not occur in a gaseous phase, but mainly on the underlying surface. This results in very little generation of particles. Additionally stated, although film deposition occurs on a heater, a susceptor, etc., the deposited films are very dense not in a flaky form to fail as particle generation sources.

(2) Good-quality films having the following properties can be obtained stably without any dependence on the O_3 concentration.

(a) The moisture content of the films is low with little moisture absorption.

(b) The insulating properties of the films are good with little leak current.

(c) The shrinkage of the films is low with low tensile stress.

(d) The etching rate of the films is constant.

(3) The step coverages of the films are in a flowing profile and any deep grooves can be filled up with the films without formation of voids. This is an advantage over any conventional processes.

(4) The film deposition rate can be raised as compared with that in the case of the conventional TEOS-O_3 process (TEOS includes one Si-

O bond in one molecule thereof.) because the polysiloxane compound to be used in the present invention includes at least two Si-O bonds in one molecule thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects, features and advantages of the present invention will be better understood from the following description taken in connection with the accomapnying drawings, in which:

Fig. 1 is a schematic illustration of production equipment for use in a CVD process in Example according to the present invention;

Fig. 2 is a diagram showing a variation of deposition rate with ozone concentration;

Fig. 3 is a diagram showing a variation of etching rate of SiO_2 film with ozone concentration;

Fig. 4 is a diagram showing a variation of shrinkage of SiO_2 film with ozone concentration;

Fig. 5 is a diagram showing a variation of stress of SiO_2 with ozone concentration;

Fig. 6 is a diagram showing an infrared absorption curve indicative of the OH group content of an SiO_2; and

Fig. 7 is an illustration comparing the step coverage of an SiO_2 film formed according to the process of the present invention with those of SiO_2 films formed according to conventional processes.

DESCRIPTION OF PREFERRED EMBODIMENTS

Fig. 1 is a schematic illustration of production equipment for use in the CVD process of Example according to the present invention, which will be given later.

The equipment of Fig. 1 comprises mass flow controllers (MFC) 2a to 2d, valves 4b to 4h, an ozone generator 6 wherein oxygen (O_2) is converted into ozone (O_3), a resorvoir 8 wherein a solution of OMCTS (octamethylcyclotetrasiloxane) is kept at a temperature of about 40 to 65 °C, a resorvoir 10 wherein a solution of TMPO (trimethyl phosphate) is kept at a temperature of about 50 to 60 °C, a resorvoir 12 wherein a solution of TEB (triethyl borate) is kept at a temperature of about 5 to 50 °C, and a CVD chamber 14.

The chamber 14 includes a heater 16, a gas outflow head 18, and a gas discharge outlet 20. Wafers 22a and 22b as substrates for film formation thereon is in place in the chamber 14.

The procedure of forming an SiO_2 film using the equipment of Fig. 1 is as follows. The valves 4a to 4d are opened. This entails generation of O_3 gas in the ozone generator 6, from which the O_3 gas is fed into the chamber 14 through the gas inflow head 18, through which OMCTS gas on a carrier gas N_2 is also fed into the chamber 14. The ensuing OMCTS-O_3 reaction forms SiO_2 films on the wafers 22a and 22b.

When PGS films are to be formed, the valves 4a to 4f are opened. This entails feeding, into the chamber 14, of O_3 gas as well as OMCTS and TMPO gases on a carrier gas N_2. The ensuing OMCTS-TMPO-O_3 reaction forms PSG films on the wafers 22a and 22b.

When BSG films are to be formed, the valves 4a to 4d, 4g and 4h are opened. This entails feeding, into the chamber 14, of O_3 gas as well as OMCTS and TEB gases on a carrier gas N_2. The ensuing OMCTS-TEB-O_3 reaction forms BSG films on the wafers 22a and 22b.

When BPSG films are to be formed, the valves 4a to 4h are opened. This entails feeding, into the chamber 14, of O_3 gas as well as OMCTS, TMPO and TEB gases on a carrier gas N_2. The ensuing OMCTS-TMPO-TEB-O_3 reaction forms BPSG films on the wafers 22a and 22b.

Example

Example according to the present invention will now be described while referring to the accompanying drawings.

Figs. 2 to 6 are diagrams showing the results of experiments on SiO_2 films formed by the CVD process of the present invention.

(1) Deposition Rate

Fig. 2 is a diagram showing the relationship between the O_3 concentration and the SiO_2 film deposition rate, wherein the abscissa represents the O_3 concentration (mol %) while the ordinate represents the deposition rate (Å/min). The temperature of the wafers (substrates) was 400 °C and the temperature of the OMCTS solution (source temperature) was 40 °C. The flow rate of the carrier gas N_2 was 4.0 SLM (standard liter/min).

In the figure, marks of white circle indicate that the underlying surface was of an Si film, while marks of black circle indicate that the underlying surface was of a thermal SiO_2 film. In either case, the deposition rate was substantially constant and stable when the O_3 concentration was 1 mol % or more. This will prove that an O_3 concentration of about 1 mol % or more can facilitate the production process control.

Under the same process conditions, the deposition rate in the process of the present invention was compared with that in the conventional TEOS-O_3 process.

- Process Conditions -

(a) substrate temperature: 400 °C
(b) source temperature: 65 °C (saturated vapor pressure: 20 mmHg)
(c) O_3 concentration: 40,000 ppm (by mol)
(d) flow rate of carrier gas N_2: 3.5 SLM

Under the above-mentioned conditions, the deposition rate in the conventional TEOS-O_3 process was 1,000 Å/min, whereas the deposition rate in the OMCTS-O_3 process according to the present invention was 2,2000 Å/min.

Thus, according to the present invention, the deposition rate is at least two times as high as that in the conventional TEOS-O_3 process to be able to improve the throughput.

(2) Etching Rate

Fig. 3 is a diagram showing the relationship between the O_3 concentration (mol %) and the etching rate (Å/min) of SiO_2 film formed by the CVD process of the present invention.

In the figure, marks of white circle indicate that the underlying surface was of an Si film, while marks of black circle indicate that the underlying surface was of a thermal SiO_2 film. In either case, the etching rate was substantially constant and stable when the O_3 concentration was 1 mol % or more. This will prove that an O_3 concentration of about 1 mol % or more can facilitate the control of an operation of etching an SiO_2 film into a patterned film.

(3) Shrinkage

Fig. 4 is a diagram showing the relationship between the O_3 concentration (mol %) and the shrinkage (%) of SiO_2 film formed by the CVD process of the present invention. The shirinkage was examined through measurement of respective film thicknesses before and after annealing (at 850 °C, for 30 sec. under N_2). In this case as well, no substantial dependence of film shrinkage on O_3 concentration was recognized. Furthermore, a very low level of film shrinkage will prove that the films were dense and of good quality.

(4) Stress

Fig. 5 is a diagram showing the relationship between the O_3 concentration and the stress of SiO_2 film formed by the CVD process of the present invention, wherein the abscissa represents the O_3 concentration (mol %) while the ordinate represents the stress (10^9 dyne/cm^2) with time being a parameter. In the figure, marks of white circle indicate that the stress was examined immediately after film deposition, while marks of white triangle indicate that the stress was examined 24 hours after the film deposition. The stress was examined through measurement of film warping.

In actual wafer processing, the value of stress examined a while after film deposition is of more significance than that examined immediately after the film deposition. In this case as well, the dependence of stress on O_3 concentration was low, and the stress values were on a low level.

(5) Moisture Content

Fig. 6 is a diagram showing an infrared absorption curve of an SiO_2 film formed by the CVD process of the present invention, wherein the abscissa represents the wavenumber (cm^{-1}) of infrared rays while the ordinate represents the relative absorption, the absolute values of which do not have any special meaning.

This curve is indicative of the moisture content of the SiO_2 film. More specifically, the absorption at around 950 cm^{-1} is assigned to OH groups constituting water molecules (H_2O). The very low absorption at around 950 cm^{-1} in the curve will prove that the SiO_2 film had a low moisture content and was of good quality with low moisture absorption.

(6) Coverage

Figs. 7 (a) to (f) compares the coverage, around a stepped portion, of an SiO_2 film formed by the CVD process of the present invention with those of SiO_2 films formed by conventional CVD processes. Such stepped portions of the underlying surface are formed when electrodes and wirings are formed.

Fig. 7 (a) illustrates the coverage of an SiO_2 film formed by the conventional SiH_4 -O_2 process, which includes constrictions around stepped portions of the underlying surface to give rise to liability to disconnection of wirings formed thereon. Fig. 7 (b) illustrates the coverage of an SiO_2 film formed by a conventional plasma process, which includes a faithful reflection of the shapes of stepped portions of the underlying surface to give rise to a downgraded reliability of wirings formed thereon.

Fig. 7 (c) illustrates the coverage of an SiO_2 film formed at an O_3 concentration of 0.6 mol % by the conventional TEOS-O_3 process, which is in an isotropic deposition profile and includes a reflection of the shapes of stepped portions of the underlying surface to give rise to liability to disconnection of wirings formed thereon.

Fig. 7 (d) illustrates the coverage of an SiO_2 film deposited at an O_3 concentration of 4 mol % by the conventional TEOS-O_3 process, which is in a flowing profile, but involves a possibility of some-

times entailing a downgraded reliability of wirings formed thereon.

Figs. 7 (e) and (f) illustrate the respective coverages of SiO_2 films deposited at O_3 concentrations of 0.6 mol % and 4 mol %, respectively, by the OMCTS-O_3 process of the present invention, which are in a flowing profile and hardly give rise to disconnection of wirings formed thereon.

As is apparent from the foregoing description, an SiO_2 film formed by the OMCTS-O_3 process of the present invention is always deposited in a flowing profile even around stepped portions of the underlying surface without any substantial dependence on the O_3 concentration to hardly give rise to liability to disconnection of wirings formed thereon. Accordingly, the process of the present invention is very effectively applicable to production of semiconductor devices with multi-layer wirings and the like.

The OMCTS-O_3 process according to the present invention was used at O_3 concentrations of 0.6 mol % and 4 mol % to form respective SiO_2 films around grooves having an aspect ratio of 5 (width: 0.8 μm, depth: 4 μm). The grooves were filled up with the respective SiO_2 films without formation of voids.

As described hereinbefore, the OMCTS-O_3 process according to the present invention is advantageous in that the film growth rate is high and substantially independent of the O_3 concentration as compared with conventional CVD processes, particularly the TEOS-O_3 process. This will advantageously raise the productivity and facilitate the production process control.

Furthermore, according to the present invention, the reaction occurs on the underlying surface to cause very little generation of particles. This can prevent a decrease in the yield of semiconductor devices, which would otherwise be attributable to particles, and can improve the reliability of semiconductor devices because of the high density and low moisture absorption of SiO_2 films formed by the process of the present invention.

An SiO_2 film formed by the process of the present invention can perfectly fill up a groove having even a high aspect ratio without formation of voids, and is in such a flowing profile even around angular parts of stepped portions of the underlying surface that wirings formed thereon hardly undergo disconnection.

Accordingly, when the CVD process of the present invention is used to form interlayer insulating films and the like, semiconductor devices with a highly reliable multi-layer wiring structure can be produced.

Claims

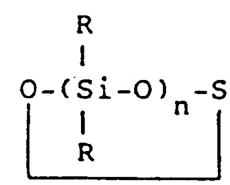
1. A process for forming a CVD film, comprising reacting a polysiloxane compound having at least two silicon-oxygen bonds with ozone to form an SiO_2 film.

2. A process for forming a CVD film as claimed in claim 1, wherein said reaction of said polysiloxane compound having at least two silicon-oxygen bonds with ozone is effected in the presence of a gas mixed therewith and containing an impurity such as phosphorus or boron to form a PSG, BSG, BPSG or like film.

3. A process for forming a CVD film as claimed in claim 1 or 2, wherein said polysiloxane compound having at least two silicon-oxygen bonds is a member selected from the group consisting of linear siloxane compounds represented by the following formula:

$$R_3Si-(\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-O)_n-SiR_3, \text{ and}$$

cyclic siloxane compounds represented by the following formula:



wherein R stands for an alkyl group which includes no hydrophilic substituent groups such as

$$-OH,\ \underset{\underset{O}{\|}}{-C}-OH,\ -CHO,$$

and

$$\underset{\underset{CH_3,}{|}}{-C=O}$$

provided that a number of R groups in one compound molecule may be the same or different

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 12 4838

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,A	EP-A-0 367 004 (T.I. INC.) * page 3, line 36 - page 2, line 3 * * page 5, lines 26 - 54; claims 1-6; figures 1, 5 *	1,3,4	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
Berlin	13 March 91	KLOPFENSTEIN P R

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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L: document cited for other reasons

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European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 12 4838

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 286 097 (AIR PRODUCTS AND CHEMICALS INC.) * page 1, lines 33 - 48 * * page 3, line 13 - page 23 * * page 4, line 18 - page 5, line 8; claims 1-10 *	1-4	H 01 L 21/316 C 23 C 16/40
Y	NEC RESEARCH AND DEVELOPMENT. no. 94, July 1989. TOKYO JP pages 1 - 7; Yasuo IKEDA et al.: "Ozone/organic-source APCVD for ULSI reflow glass films" * page 1, right-hand column - page 2 * * Photos 1,2 *	1-4	
A	US-A-4 168 330 (GRZEGORZ KAGANOWICZ ET AL.) * column 1, line 64 - column 2, line 12 * * column 4, line 15 - column 26; claims 1, 2 *	1,3,4	
A	EXTENDED ABSTRACTS OF THE 1988 FALL MEETING, CHICAGO, ILLINOIS vol. 88-2, 09 October 1988, Princeton, NEW JERSEY pages 335 -336; A.K. HOCHBERG et al.: "Silicon oxide deposition from cyclic siloxane precursors" * the whole document *	1-4	
A	EXTENDED ABSTRACTS OF THE 19th. CONFERENCE ON SOLID STATE DEVICES AND MATERIALS, TOKYO 25 August 1987, pages 447 - 450; Y. NISHIMOTO et al.: "Low temperature chemical vapor deposition of dielectric films using ozone and organosilane" * page 447, right-hand column * * page 450 * * photos 2,3, table 1 *	1-4	TECHNICAL FIELDS SEARCHED (Int. Cl.5) H 01 L C 23 C
A	PROCEEDINGS OF THE 1989 VMIC CONFERENCE 12 June 1989, pages 382 - 389; Y. NISHIMOTO et al.: "Dielectric film deposition by atmospheric pressure and low temperature CVD using TEOS, ozone and new organometallic doping sources" * pages 383 - 384 *	1,2,4	

-/-

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
Berlin	13 March 91	KLOPFENSTEIN P R

CATEGORY OF CITED DOCUMENTS

- X: particularly relevant if taken alone
- Y: particularly relevant if combined with another document of the same catagory
- A: technological background
- O: non-written disclosure
- P: intermediate document
- E: earlier patent document, but published on, or after the filing date
- D: document cited in the application
- L: document cited for other reasons
- &: member of the same patent family, corresponding document

FIG. 7(a)

SiH_4-O_2 PROCESS

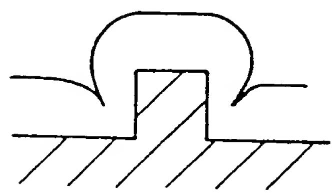


FIG. 7(b)

PLASMA PROCESS

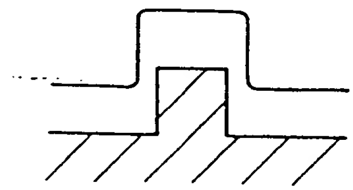


FIG. 7(c)

TEOS PROCESS
(O_3 CONCENTRATION 0.6%)

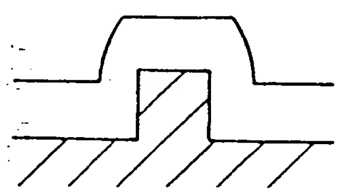


FIG. 7(d)

TEOS PROCESS
(O_3 CONCENTRATION 4%)

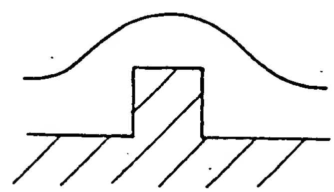


FIG. 7(e)

OMCTS PROCESS
(O_3 CONCENTRATION 0.6%)

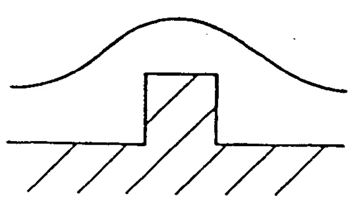


FIG. 7(f)

OMCTS PROCESS
(O_3 CONCENTRATION 4%)

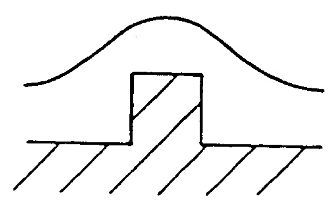


FIG.6

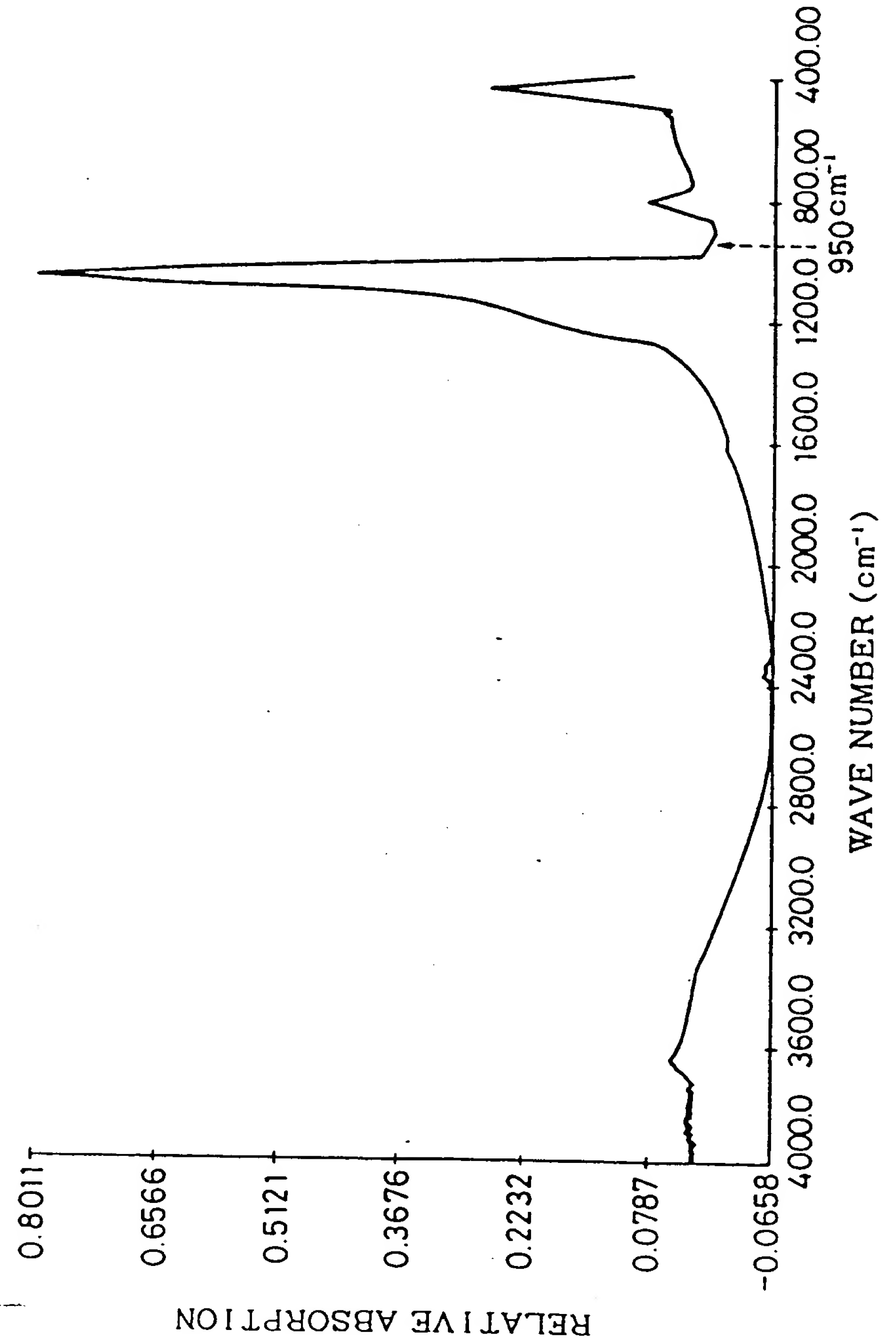

RELATIVE ABSORPTION
0.8011
0.6566
0.5121
0.3676
0.2232
0.0787
-0.0658
4000.0
3600.0
3200.0
2800.0
2400.0
2000.0
1600.0
1200.0
800.00
400.00
950cm⁻¹
WAVE NUMBER (cm⁻¹)

FIG. 5

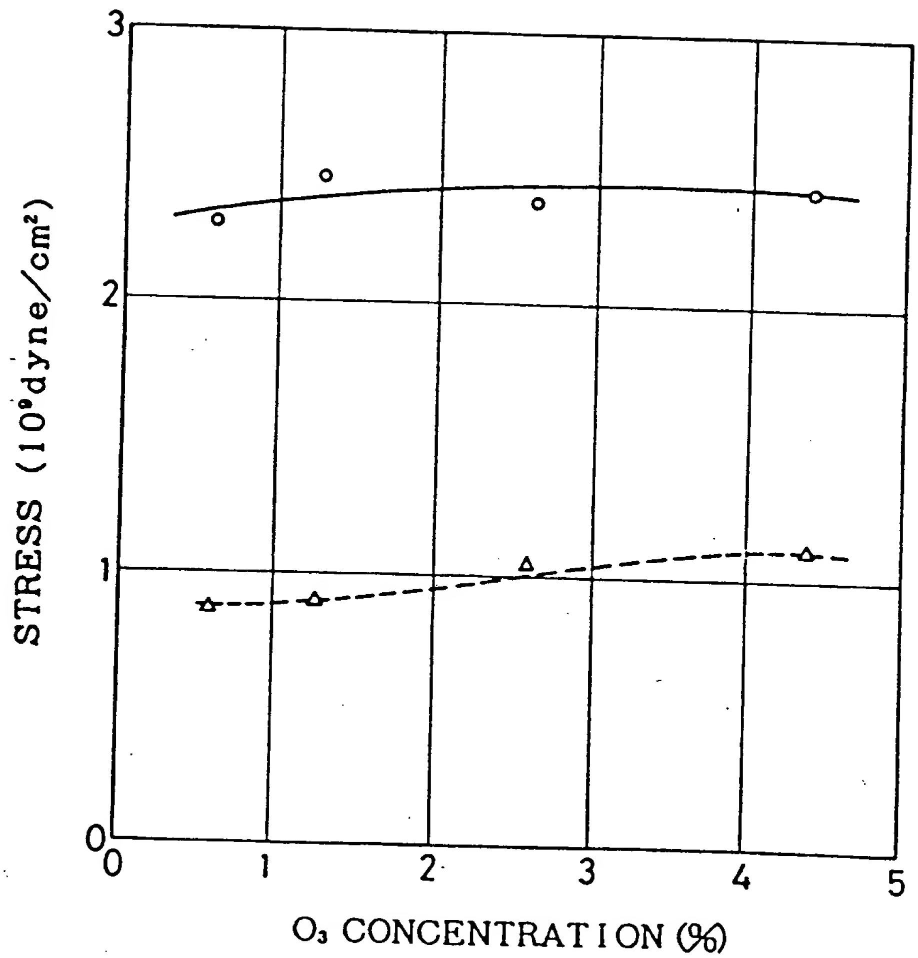


FIG. 3

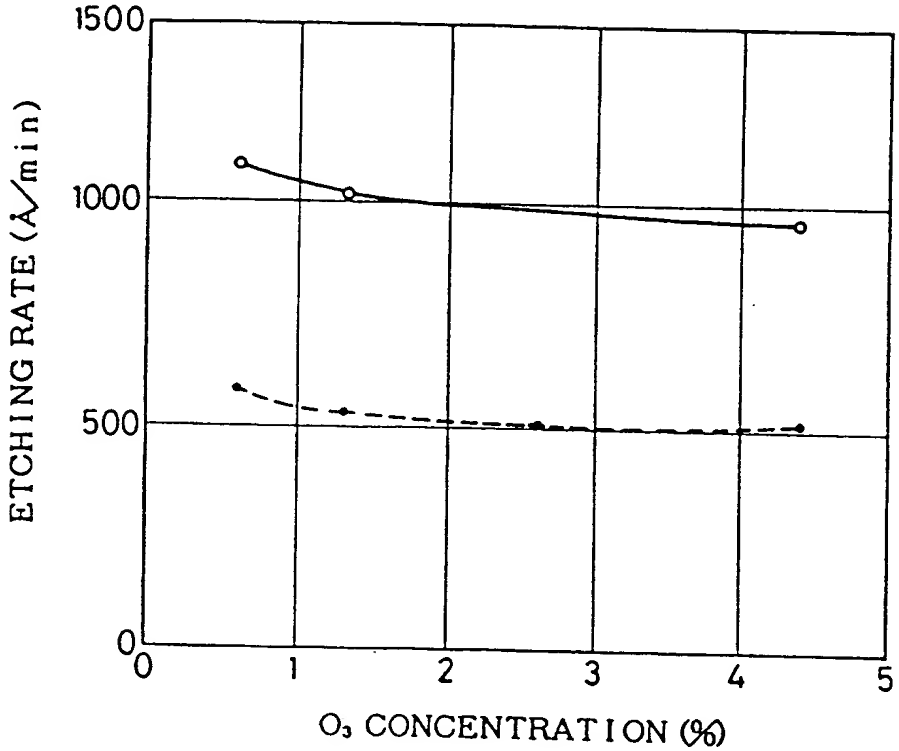

1500
1000
500
0
ETCHING RATE (Å/min)
0
1
2
3
4
5
O3 CONCENTRATION (%)

FIG. 4

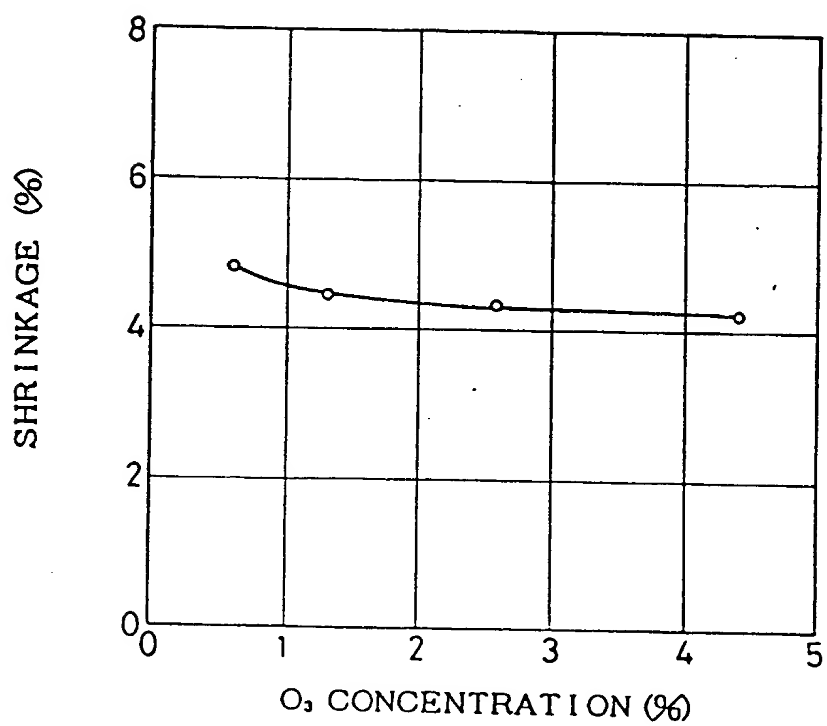
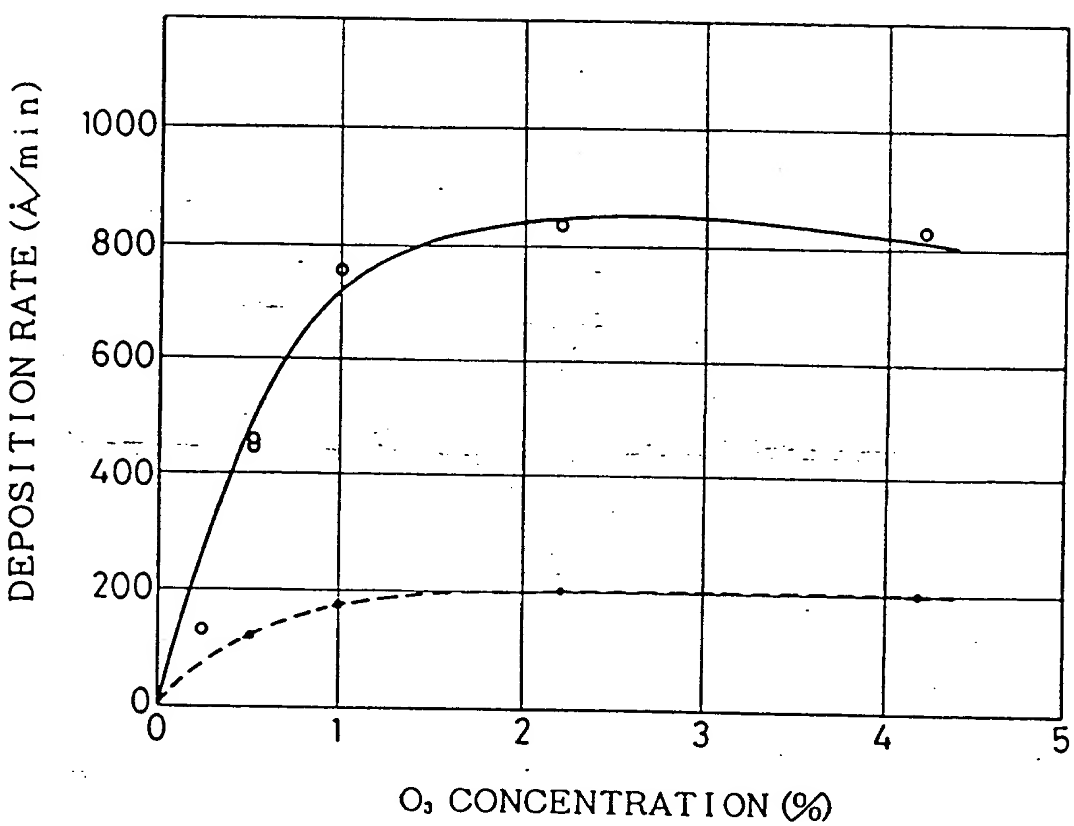
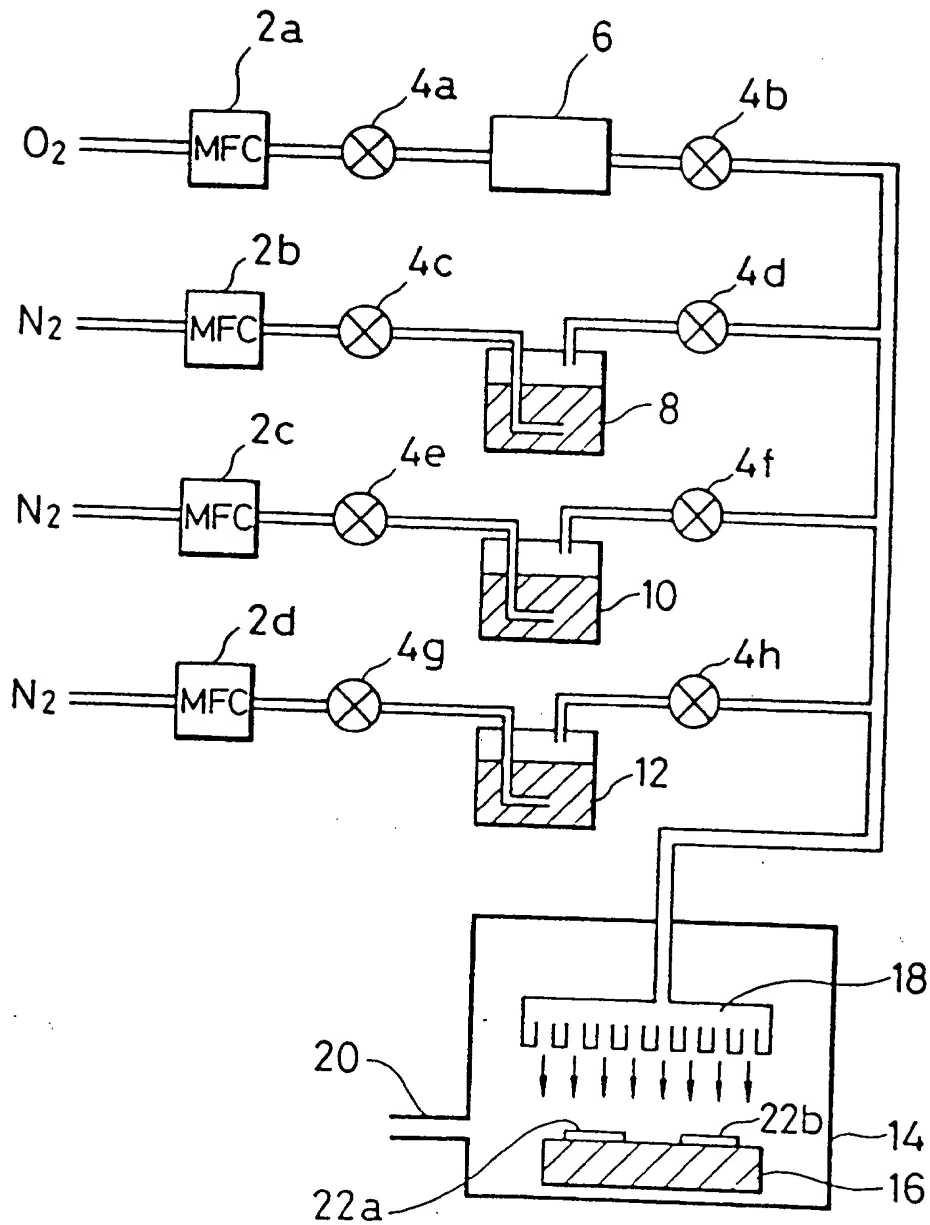

8
6
4
2
0
SHRINKAGE (%)
0
1
2
3
4
5
O3 CONCENTRATION (%)

FIG. 2


DEPOSITION RATE (Å/min)
1000
800
600
400
200
0
0
1
2
3
4
5
O_3 CONCENTRATION (%)

4. A semiconductor device comprising an SiO_2 film as set forth in claim, or a PSG, BSG, BPSG or like film as set forth in claim 2, which is formed as a planarizing film, an interlayer insulating film, or a cover insulating film.

FIG. 1


2a
6
4a
4b
O_2
MFC
2b
4c
4d
N_2
MFC
8
2c
4e
4f
N_2
MFC
10
2d
4g
4h
N_2
MFC
12
18
20
22b
14
22a
16